PCT

WORLD INTELLECTUAL PROPERTY ORGANIZATION
International Bureau

INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification 5 : B01J 8/02, C07B 41/04, C07C 1/04, 27/06, 29/152, F28D 7/02

A1

(11) International Publication Number: WO 94/12274

(43) International Publication Date: 9 June 1994 (09.06.94)

(21) International Application Number: PCT/EP93/03252

(22) International Filing Date: 18 November 1993 (18.11.93)

(30) Priority Data:
92203589.4 20 November 1992 (20.11.92) EP
(34) Countries for which the regional or international application was filed: GB et al.

(71) Applicant *(for CA only)*: SHELL CANADA LIMITED [CA/CA]; 400-4th Avenue S.W., Calgary, Alberta T2P 2H5 (CA).

(71) Applicant *(for all designated States except CA)*: SHELL INTERNATIONALE RESEARCH MAATSCHAPPIJ B.V. [NL/NL]; Carel van Bylandtlaan 30, NL-2596 HR The Hague (NL).

(72) Inventors: SIE, Swan, Tiong; Badhuisweg 3, NL-1031 CM Amsterdam (NL). EILERS, Jacobus; Badhuisweg 3, NL-1031 CM Amsterdam (NL).

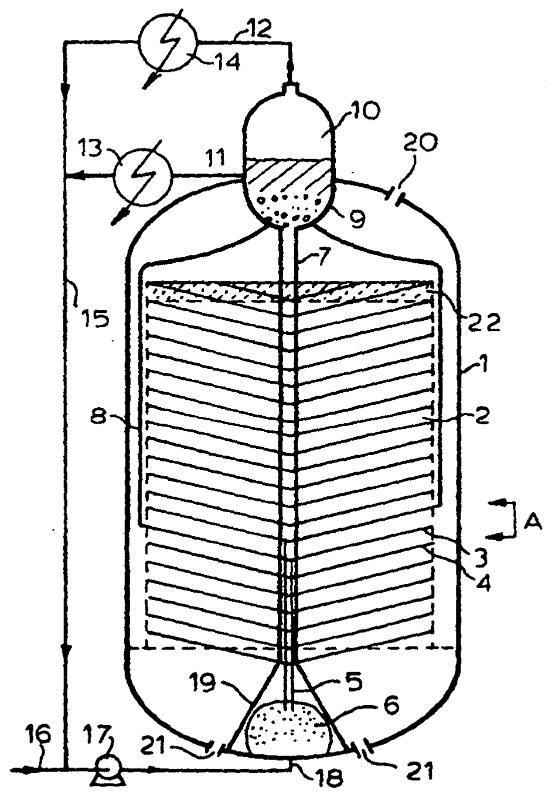
(81) Designated States: AT, AU, BB, BG, BR, BY, CA, CH, CZ, DE, DK, ES, FI, GB, HU, JP, KP, KR, KZ, LK, LU, MG, MN, MW, NL, NO, NZ, PL, PT, RO, RU, SD, SE, SK, UA, VN, European patent (AT, BE, CH, DE, DK, ES, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, ML, MR, NE, SN, TD, TG).

Published
With international search report.

(54) Title: REACTOR AND PROCESS FOR HIGHLY EXOTHERMIC OR ENDOTHERMIC REACTIONS

(57) Abstract

The present invention relates to a reactor comprising a normally vertical reactor vessel (1) comprising a reaction zone (2) for retaining a bed of catalyst and a plurality of heat-exchange means (3, 4) spaced apart in a vertical direction within the reaction zone, each heat-exchange means having an enveloppe, converging in a vertical direction, wherein the enveloppe is defined by the outer surface of one or more tubes. Adjacent heat-exchange means are offset about the axis of the reactor vessel, in every pair of adjacent heat-exchange means, the angle of offset between the said means preferably being the same. The reaction zone preferably comprises a fixed catalyst bed. The present invention further relates to processes involving highly exothermic or endothermic reactions, which highly exothermic or endothermic reactions are carried out in a reactor according to the present invention.



FOR THE PURPOSES OF INFORMATION ONLY

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AT	Austria	GB	United Kingdom	MR	Mauritania
AU	Australia	GE	Georgia	MW	Malawi
BB	Barbados	GN	Guinea	NE	Niger
BE	Belgium	GR	Greece	NL	Netherlands
BF	Burkina Faso	HU	Hungary	NO	Norway
BG	Bulgaria	IE	Ireland	NZ	New Zealand
BJ	Benin	IT	Italy	PL	Poland
BR	Brazil	JP	Japan	PT	Portugal
BY	Belarus	KE	Kenya	RO	Romania
CA	Canada	KG	Kyrgystan	RU	Russian Federation
CF	Central African Republic	KP	Democratic People's Republic of Korea	SD	Sudan
CG	Congo			SE	Sweden
CH	Switzerland	KR	Republic of Korea	SI	Slovenia
CI	Côte d'Ivoire	KZ	Kazakhstan	SK	Slovakia
CM	Cameroon	LI	Liechtenstein	SN	Senegal
CN	China	LK	Sri Lanka	TD	Chad
CS	Czechoslovakia	LU	Luxembourg	TG	Togo
CZ	Czech Republic	LV	Latvia	TJ	Tajikistan
DE	Germany	MC	Monaco	TT	Trinidad and Tobago
DK	Denmark	MD	Republic of Moldova	UA	Ukraine
ES	Spain	MG	Madagascar	US	United States of America
FI	Finland	ML	Mali	UZ	Uzbekistan
FR	France	MN	Mongolia	VN	Viet Nam
GA	Gabon				

REACTOR AND PROCESS FOR HIGHLY EXOTHERMIC OR ENDOTHERMIC REACTIONS

The present invention relates to a reactor which can be used for carrying out highly exothermic or endothermic reactions. Especially, the present invention relates to a reactor containing heat-exchange means. The present invention further relates to the use of the reactor in processes involving highly endothermic or highly exothermic reactions.

A well-known reactor suitable for use in processes involving highly endothermic or exothermic reactions, is the so-called multi-tubular reactor, such as disclosed in European patent specification No. 308 034. A plurality of long tubes with small diameter is filled with catalyst particles. The tubes are surrounded by heating or cooling gas or liquid, to ensure a good heat-transfer coefficient between the reactants and products in the tube and the heating or cooling gas or liquid outside the tubes.

A disadvantage of the multi-tubular reactor is that upscaling of the reactor, to increase the capacity thereof, is difficult and expensive.

In British patent specification No. 2 204 055 (GB 2 204 055), a different type of reactor is described for use in the highly exothermic process of converting synthesis gas into hydrocarbons of at least two carbon atoms. The reactor comprises a plurality of helically-wound tube bundles, concentrically arranged around a central tube. In contrast to the multi-tubular reactor, the tubes are filled with cooling medium and the free space between the tubes is filled with catalyst particles. Typically, adjacent helically-wound tube bundles have opposite screw-directions. While this reactor solves some problems associated with the multi-tubular reactor, there is still a need for further improvement. A drawback of the reactor described in GB 2 204 055 is that the reactants can

flow through straight unobstructed passages in the space between adjacent tube bundles. Heat generated in these passages has to be transferred sideways to the tube surfaces, which lowers the heat transfer coefficient, and, hence, efficient heat-removal. Another drawback is that this flow of reactants through the unobstructed passage results in little mixing between flows through adjacent unobstructed passages. Hence, maldistributions of flow may persist in large parts of the reactor.

United States patent specification No. 5,080,872 (US 5,080,872) describes a reactor comprising flat pancake-shaped spirals of cooling tubes, which spirals are arranged substantially transverse to the reactant flow through the reactor. Adjacent spirals are in spaced relationship relative to each other around the longitudinal axis of the reactor. Since adjacent spirals have a different screw-direction, unobstructed passages in the axial direction of the reactor are prevented. While the problems associated with unobstructed passages in axial direction in the reactor described in GB 2 204 055 are solved, some other problems are created. When the reactor described in US 5,080,872 is to be cooled with a boiling liquid, for example boiling water, stagnant steam bubbles may form in the flat spirals, which may give rise to an undesired temperature profile in the reactor.

Accordingly, it would be desirable to be able to operate highly exothermic or endothermic reactions in a reactor which does not suffer from disadvantages associated with reactors described in the prior art. Further, it would be desirable to be able to provide a reactor having an optimal heat-transfer coefficient.

It has now surprisingly been found that the poor performance arising from problems associated with known reactors can be significantly improved by a reactor comprising a plurality of heat-exchange means of a specific shape, for example a cone or bowl shape.

Accordingly, the present invention relates to a reactor comprising a normally vertical reactor vessel comprising a reaction zone for retaining a bed of catalyst and a plurality of heat-

exchange means spaced apart in a vertical direction within the reaction zone, each heat-exchange means having an envelope, converging in a vertical direction, wherein the envelope is defined by the outer surface of one or more tubes.

The reactor of the present invention is typically a cylindrical vessel, which in use is normally arranged vertically. Typically, the length of the vessel (corresponding in normal use to its height) is greater than the diameter. The features of the reactor will be further described with reference to the reactor as vertically arranged in normal use.

The heat-exchange means may be of any design, provided the envelope of the heat-exchange means converges in a vertical direction. Examples of suitable designs include heat-exchange means comprising hairpin-shaped tubes, single and double spiral-wound tubes.

It will be understood that the term tube as used in the present application is not limited to tubes having a circular shape in cross-section. If desired, tubes may have an oval, a triangular, a square or other shape in cross-section.

The envelope of the heat-exchange means may converge in a vertical direction in a continuous or a discontinuous (irregular) way. For example, the envelope may converge step-wise in a vertical direction. However, the envelope of the heat-exchange means preferably converges continuously in a vertical direction. If the envelope converges continuously, it is easier to prevent the distance between two adjacent tubes of adjacent heat-exchange means from becoming too large to ensure efficient heat transfer. This is of particular importance if the reactor of the present invention is used for carrying out highly exothermic reactions which are not thermodynamically limited at high temperatures. An example of such a highly exothermic reaction is the conversion of synthesis gas into paraffinic hydrocarbons, commonly known as a Fischer-Tropsch synthesis reaction.

In one embodiment, the continuously converging envelope of the heat-exchange means describes a cone-shape, hereinafter a cone-

shaped heat-exchange means. In another embodiment, the continuously converging envelope has a convex curvature when the heat-exchange means is viewed in a vertical cross-section. Accordingly, the envelope describes a bowl-shape, hereinafter a bowl-shaped heat-exchange means. In yet another embodiment, the continuously converging envelope describes a concave curvature when the heat-exchange means is viewed in a vertical cross-section.

Preferably, the heat-exchange means are arranged along the vertical axis of the reactor vessel. The heat-exchange means may be spaced at equal distances from each other, but the distance may also be varied in the vertical direction of the reactor, depending upon whether it is desired to operate at the same or a different reactor temperature at the top and at the bottom of the reaction zone. For example, if it is desired to convert synthesis gas into hydrocarbons of at least two carbon atoms in a reactor according to the present invention, it is desirable to operate the reactor at a relatively low temperature at the top of the reaction zone and a higher temperature at the bottom of the reaction zone. If it is desired to prepare methanol from synthesis gas, the reverse may be desired. It is to be understood that other means for varying the reactor temperature in a vertical direction may also be applied. Examples include connecting different heat-exchange means to different heat-exchange medium supply means or filling the reaction zone with a catalyst mixture comprising a varying amount of inert material, such as silicon carbide.

Unobstructed passages in the reaction zone may be prevented by employing adjacent heat-exchange means of different shape. However, for ease of manufacture, the heat-exchange means are preferably of substantially the same shape and dimension. Unobstructed passages are then typically prevented by offsetting adjacent heat-exchange means about the axis of the reactor vessel. Preferably, in every pair of adjacent heat-exchange means, the angle of offset between the said means is the same.

Typically, adjacent heat-exchange means are offset by an angle of rotation of from 5 to 180°. The most preferred angle of rotation

depends on the design of the heat-exchange means. If the heat-exchange means is formed by spiral-wound tubes, adjacent heat-exchange means are preferably offset by about 180°. If the heat-exchange means is formed by hairpin-shaped tubes, adjacent heat-exchange means are preferably offset by about 10°. It is to be understood that this angle of rotation may be a left-hand or a right-hand rotation and a left-hand rotation of 190° is equal to a right-hand rotation of 170°.

It will be understood that the heat-exchange means may have any suitable size and heat-exchange means may be arranged so as to avoid unobstructed passages. However, for ease of manufacture and ease of operating the reactor, it is preferred that each heat-exchange means extends across substantially the entire reaction zone in a radial direction.

The envelope of each heat-exchange means may converge in either vertical direction. Preferably, the heat-exchange means converge in the same direction.

Preferably, the heat-exchange means present in the reactor vessel, are equipped with heat-exchange medium inlet means at the lower end of the heat-exchange means and heat-exchange medium outlet means at the upper end of the heat-exchange means. This arrangement is particularly preferred when the reactor is to be used for carrying out exothermic reactions. Accordingly, in case, for example, the reactor vessel comprises heat-exchange means having an envelope converging to the bottom of the reactor vessel, the heat-exchange medium inlet means are located in the region of the vertical axis the reaction zone, and the heat-exchange medium outlet means are located in the region of the periphery of the reaction zone.

In a preferred embodiment, the envelope of the heat-exchange means is formed by one or more spiral-wound tubes.

Typically, the reaction zone, in operation, contains a catalyst bed of solid catalyst particles. In principle, any catalyst bed may be present in the reaction zone, such as a fluidized bed, a moving bed, slurry phase bed and a fixed catalyst

bed. However, especially in case the reaction zone comprises a fluidized catalyst bed, the heat-exchange means have to be made of materials highly resistant to abrasion. Preferably, the reaction zone contains a fixed catalyst bed.

It will be appreciated that if the reactor is to be used for carrying out highly exothermic reactions, cooling medium is present in the heat-exchange means. A large variety of cooling media known to persons skilled in the art may be applied. Examples include inert gases, steam, boiling water, pressurised water and suitable cooling oils. Which cooling medium is preferred depends upon, inter alia, the process that is carried out in the reactor. It lies within the skill of the skilled person to select the most suitable cooling medium for use in the reactor of the present invention.

If the reactor is to be used for carrying out highly endothermic reactions, it will be appreciated that heating medium is present in the heat-exchange means. A large variety of heating media known to persons skilled in the art may be applied. Examples include inert gases, steam, boiling water, pressurised water, molten salts and suitable oils. Which heating medium is preferred depends upon, inter alia, the process that is carried out in the reactor. It lies within the skill of the skilled person to select the most suitable heating medium for use in the reactor of the present invention.

Embodiments of the reactor of the present invention will be described with reference to the accompanying Figures, in which:

Figure 1 is a schematic vertical cross-sectional view of a preferred reactor comprising cone-shaped heat-exchange means, for use in a highly exothermic reaction comprising converting synthesis gas into at least partly liquid hydrocarbons;

Figure 2 is a schematic representation of two cone-shaped heat-exchange means, viewed in direction A in Figure 1;

Figure 3 is a schematic representation of the two cone-shaped heat-exchange means of Figure 2, viewed in the vertical direction B;

Figure 4 is a schematic representation of one bowl-shaped heat-exchange means viewed in vertical cross-section;

Figures 5 and 6 are schematic representations of the plan view of different bowl-shaped heat-exchange means;

Figure 7 is a schematic representation of the bowl-shaped heat-exchange means of figure 5, viewed in direction C; and

Figure 8 is a schematic representation of one heat-exchange means having a continuously converging envelope, wherein the envelope describes a concave curvature.

Figure 1 shows a reactor, comprising a normally vertical reactor vessel 1, the walls of which define a reaction zone 2 and in which a plurality of cone-shaped spiral-wound heat-exchange means (two of which have been identified by the numerals 3 and 4), schematically represented by a 'v-shape' in Figure 1. A more detailed drawing of heat-exchange means 3 and 4 can be found in Figures 2 and 3. Referring again to Figure 1, cooling medium such as boiling water, is introduced into the heat-exchange means via lines 5, connected at their lower ends to a bowl-shaped tube sheet 6 in the lower domed-end portion of the reactor vessel 1. The lines 5 are retained within a central tube 7, which serves as a structural member, at the lower end sealed to a cone-shaped member 19 in the lower domed-end portion of the reactor vessel 1. Cooling medium is withdrawn from the heat-exchange means via lines 8, connected to a bowl-shaped tube sheet 9. The tube sheet 9 is in communication with a cooling medium trap 10. A gaseous cooling medium, such as steam, is vented into the air or, preferably, sent to recycle via a line 12, a heat-exchanger 14 and a line 15. A liquid cooling medium is sent to recycle via a line 11, a heat-exchanger 13 (if required) and line 15. Make-up cooling medium is introduced via line 16 and cooling medium is introduced into the heat-exchange means 3, 4 inside the reactor vessel via a pump 17, line 18, the tube sheet 6 and lines 5. Synthesis gas is introduced into the reactor vessel 2 via a gas inlet means 20. Product is withdrawn from reactor vessel 2 via a product outlet means 21. In order to ensure homogeneous introduction of synthesis gas in the

reaction zone 2, an inert layer 22, typically silicon carbide, may be provided in the upper of the reaction zone 2.

For simplicity, Figure 1 shows only those lines connecting the heat-exchange means 3, 4 with the bowl-shaped tube sheets 6 and 9. It will be appreciated that similar lines are provided connecting the remaining heat-exchange means to the aforementioned tube sheets in like manner.

Figure 2 shows two vertically stacked cone-shaped spiral-wound heat-exchange means 3 and 4, wherein the heat-exchange means 3 is offset by 180° with respect to the heat-exchange means 4. Preferably, as shown in Figure 2, the tubes 40 of heat-exchange means 4 each have the same angle α with respect to the vertical axis 50 of the reactor vessel. The tubes 30 of the heat-exchange means 3 preferably each have the same angle β with respect to the vertical axis 50 of the reactor vessel, which angle is equal to $(180° - \alpha)$. Typically, α may vary from 70° to 89°. It is to be understood that α and β are not necessarily constant over the heat-exchange means and are a function of the desired cooling or heating surface per unit reactor volume, and the desired shape of the heat-exchange means.

The distance x between the tubes 40 may typically be in the range of from 10 to 200 mm, especially from 10 to 50 mm. The diameter of the tubes 40 is typically in the range of from 4 to 55 mm, especially from 10 to 35 mm.

Figure 3 shows the two vertically stacked cone-shaped spiral-wound heat-exchange means 3 and 4 of Figure 2. viewed in direction B. It can be seen that spiral-wound heat-exchange means 3 is offset by 180° about the vertical axis 50, with respect to heat-exchange means 4. The radial distance y between tubes 30 and 40 may range from 10 to 50 mm, preferably from 15 to 25 mm.

Figure 4 shows an alternative to the cone-shaped heat-exchange means. In this embodiment a spiral-wound tube 65 forms a bowl-shaped heat-exchange means 60, which heat-exchange means is equipped with a heat-exchange medium inlet 5 and a heat-exchange medium outlet 8.

Figures 5 and 6 show further alternatives to the cone-shaped heat-exchange means. In the embodiment of Figure 5 a hairpin-shaped tube 70 forms a bowl-shaped heat-exchange means 75, which heat-exchange means is equipped with a heat-exchange medium inlet 5 and a heat-exchange medium outlet 8. In the embodiment of Figure 6 a double spiral-wound tube 80 forms a bowl-shape heat-exchange means 85, which heat-exchange means is equipped with a heat-exchange medium inlet 5 and a heat-exchange medium outlet 8.

Figure 7 shows the bowl-shape of the heat-exchange means 75, when viewed in direction C in Figure 5.

Figure 8 shows a heat-exchange means 95 comprising a spiral-wound tube 90, defining an envelope 96 which describes a concave curvature when viewed in a vertical cross-section of the heat-exchange means. The heat-exchange means is equipped with a heat-exchange medium inlet 5 and a heat-exchange medium outlet 8.

It is to be understood that Figures 1 to 8 are simplified schemes of certain embodiments of the reactor according to the present invention. Apparatus, such as additional pumps, catalyst inlet means and catalyst outlet means, have been omitted for the sake of clarity, but will be apparent to those skilled in the art.

The present invention further relates to processes involving highly exothermic or endothermic reactions, which reactions are carried out in a reactor as described hereinbefore.

In one embodiment, the present invention relates to a process involving a highly exothermic reaction, which reaction is carried out in a reactor as described hereinbefore, which reactor comprises a reaction zone containing a fixed catalyst bed.

Preferably, the highly exothermic reaction comprises reacting a synthesis gas feed at elevated temperature and pressure in the presence of a catalyst to lower alcohols, such as methanol, ethers, aromatic hydrocarbons and/or aliphatic hydrocarbons. More preferably the highly exothermic reaction comprises reacting a synthesis gas feed, having a typical H_2/CO molar ratio of up to 2.5 in the presence of a Fischer-Tropsch catalyst. Typical reaction conditions are a temperature in the range of from 125 °C to 350 °C

and a pressure in the range of from 5 to 100 bar abs. Preferred catalysts for use in the process are catalysts comprising a metal chosen from the group of cobalt, iron or nickel, more preferably cobalt. The process typically yields highly paraffinic hydrocarbons.

In another preferred embodiment the highly exothermic reaction comprises reacting ethylene with molecular oxygen in the presence of a silver-containing catalyst.

In another embodiment, the present invention relates to a process involving a highly endothermic reaction, which reaction is carried out in a reactor as described hereinbefore, which reactor comprises a reaction zone containing a fixed catalyst bed.

Typically, the highly endothermic reaction may comprise the catalytic dehydrogenation of light hydrocarbons, such as C_3-C_5 paraffins, to olefins, in the presence of a noble metal containing catalyst. In another embodiment, the highly endothermic reaction may comprise the catalytic reforming of a gasoline boiling range hydrocarbon feed, in the presence of a noble metal containing catalyst.

It will be understood that reactants may be introduced in either the top or bottom of the reaction zone and products may be withdrawn from the bottom or top of the reaction zone.

A typical process scenario comprising the conversion of a synthesis gas feed to highly paraffinic hydrocarbons would proceed as follows.

A mixture of hydrogen and carbon monoxide (H_2/CO ratio = 1.1) is fed to a reactor as depicted in Figure 1. The reaction zone comprises a fixed bed of a catalyst comprising cobalt (18.3 %wt., calculated as cobalt oxide), zirconium (8.5 %wt., calculated as zirconium oxide) and silica. The catalyst is prepared by a process as described in European patent application publication No. 428 223. The reactor is operated at a temperature of about 210-225 °C, a pressure of 36 bar and a gas hourly space velocity of 1125 $Nl.l^{-1}.h^{-1}$. A conversion is obtained of about 75% of CO to hydrocarbons of at least two carbon atoms.

CLAIMS

1. Reactor comprising a normally vertical reactor vessel comprising a reaction zone for retaining a bed of catalyst and a plurality of heat-exchange means spaced apart in a vertical direction within the reaction zone, each heat-exchange means having an envelope, converging in a vertical direction, wherein the envelope is defined by the outer surface of one or more tubes.

2. Reactor according to claim 1, wherein each heat-exchange means has an envelope continuously converging in a vertical direction.

3. Reactor according to claim 1 or 2, wherein the heat-exchange means are arranged along the vertical axis of the reactor vessel.

4. Reactor according to claim 3, wherein adjacent heat-exchange means are offset about the vertical axis of the reactor vessel, in every pair of adjacent heat-exchange means, the angle of offset between the said means preferably being the same.

5. Reactor according to claim 4, wherein adjacent heat-exchange means are offset by 5-180°.

6. Reactor according to any one of the preceding claims, wherein the reactor vessel, the heat-exchange means are equipped with a heat-exchange medium inlet at the lower end of the heat-exchange means and a heat-exchange medium outlet at the upper end of the heat-exchange means.

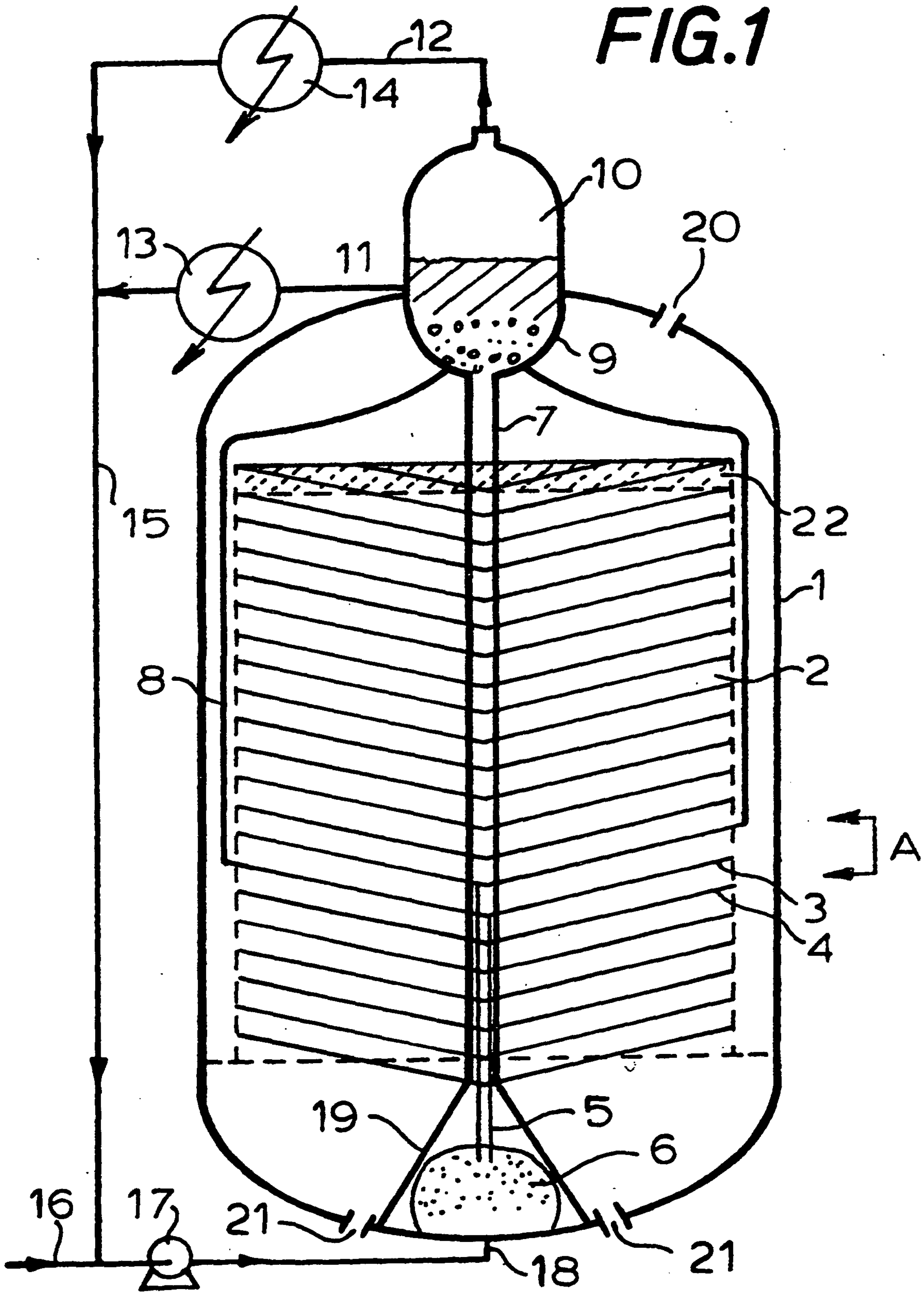
7. Reactor according to any one of the preceding claims, wherein the heat-exchange means are formed by one or more spiral-wound tubes.

8. Reactor according to any one of the preceding claims, wherein the reaction zone contains a catalyst bed of solid catalyst particles, preferably a fixed catalyst bed.

9. Process comprising a highly exothermic reaction which highly exothermic reaction is carried out in a reactor as claimed in any one of claims 1 to 8.

10. Process according to claim 9, wherein the highly exothermic reaction comprises reacting a synthesis gas feed at elevated temperature and pressure in the presence of a catalyst to lower alcohols, ethers, aromatic hydrocarbons and/or aliphatic hydrocarbons.

FIG.1



SUBSTITUTE SHEET

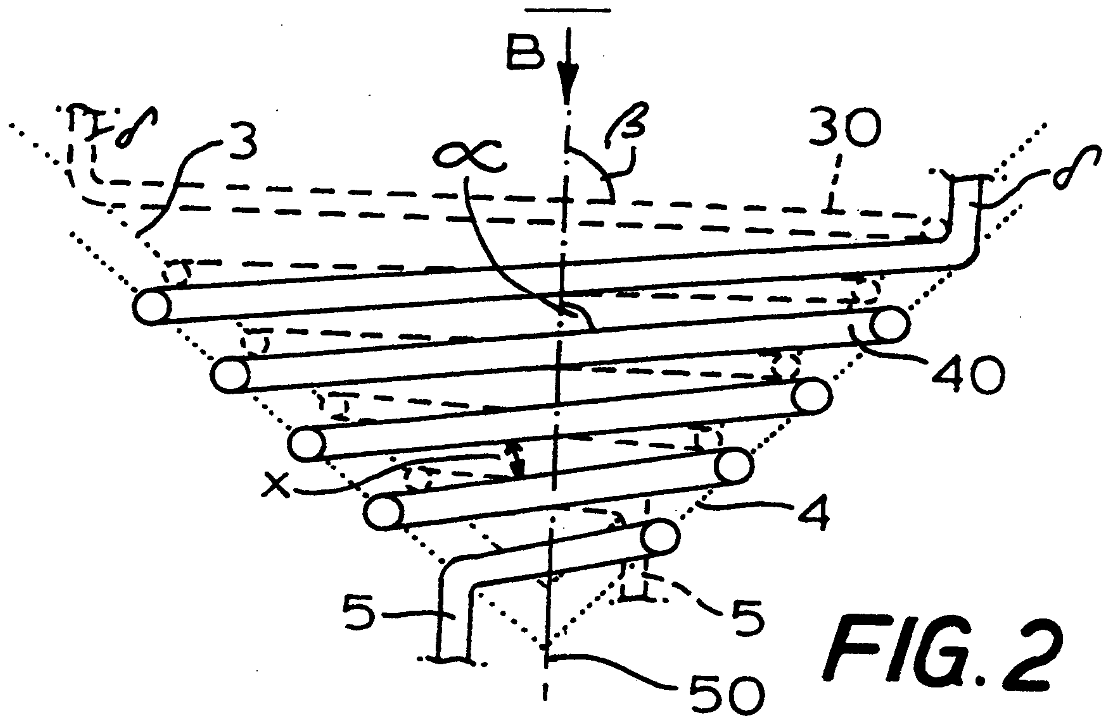


FIG. 2

FIG. 3

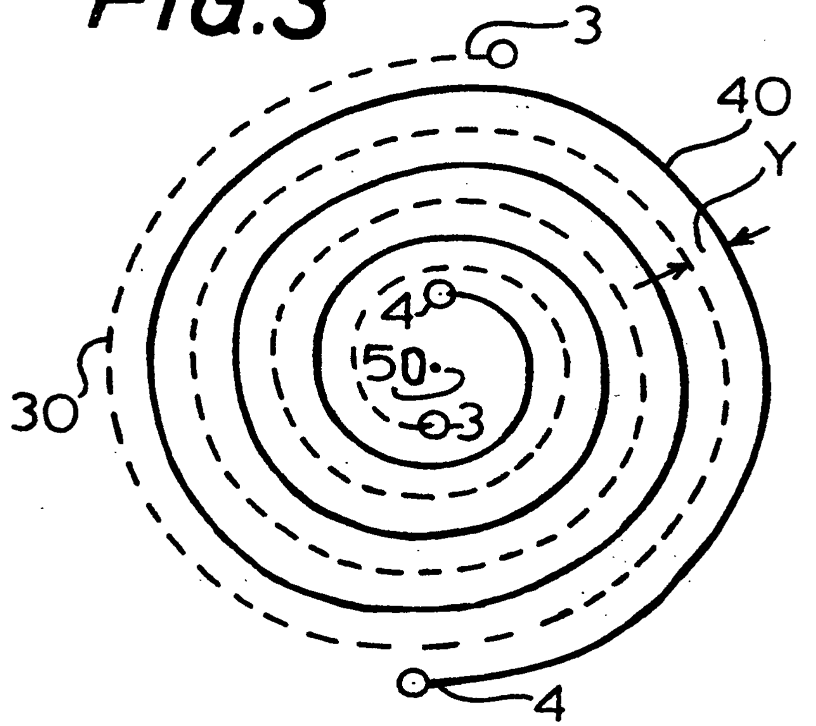


FIG. 4

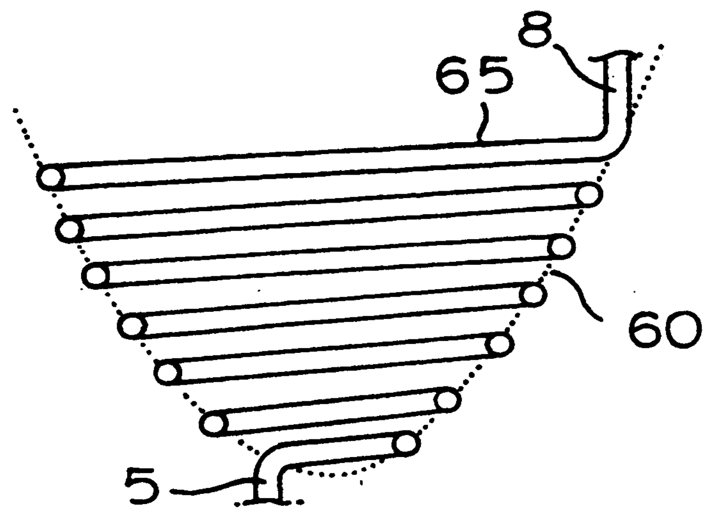


FIG. 5

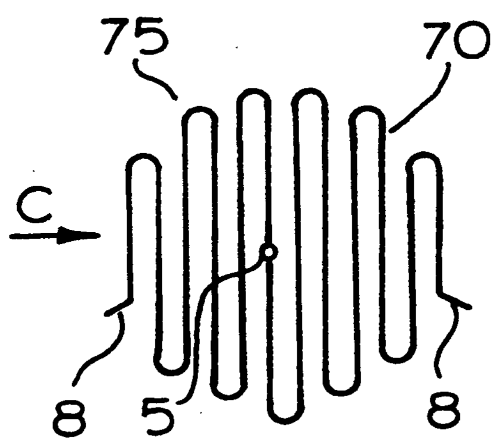


FIG. 6

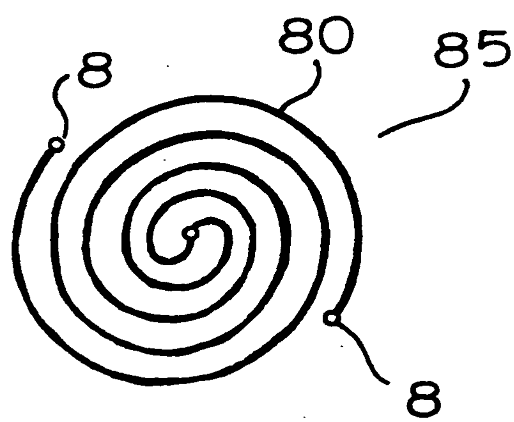


FIG.7

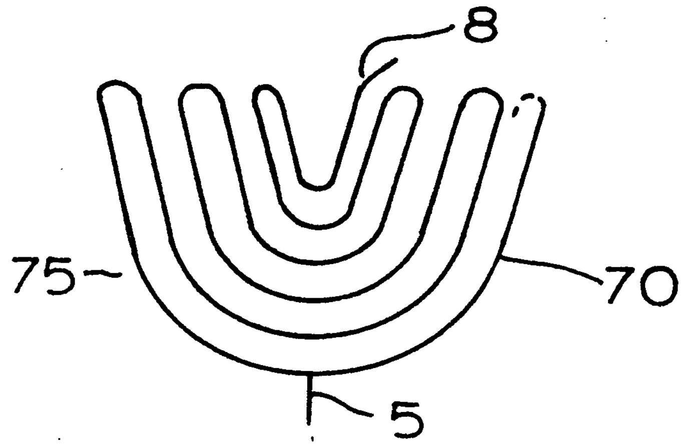


FIG.8